Technical Paper

Phase-Field Approach - A Paradigm Shift in Metallurgical Solidification Modelling

S. K. Das and K. M. Godiwalla*

This paper provides a fundamental overview of the phase field theory addressing some of the basic concepts, modelling formalism and application of phase field approach in metallurgical solidification analysis. The main advantage of the phase field method is that the location of the solid-liquid interface is given implicitly by the phase field, which greatly simplifies the handling of merging interfaces. The phase field methods have become increasingly popular in numerical simulation over the past ten years. Using a phase-field variable and a corresponding governing equation to describe the state (solid or liquid) in a material as a function of position and time, the diffusion equations for heat and solute can be solved without tracking the liquid-solid interface. The interfacial regions between liquid and solid involve smooth but highly localised variations of the phase-field variable. It is indeed a paradigm shift in metallurgical solidification analysis and modelling. The technique has been applied a wide variety of problems by various researchers including dendritic growth in pure materials; dendritic, eutectic, and peritectic growth in alloys; and solute trapping, rapid solidification and continuous casting operation.

Introduction

In classical approach of metallurgical casting and solidification modelling and analysis, there is typically a solid phase and a liquid phase, separated by a thin solidification front. This interface has associated with it, for example, surface energy , and is the location of latent heat release during solidification. Solutions to such models in conjunction with experimental results provide a wealth of insight into the understanding of physical phenomena. However, since the interface position must be determined as part of the solution, often only solutions with very special interface shapes (e.g. planar, spherical, nearly planar, or nearly spherical) can be obtained. Solutions become exceedingly difficult to obtain as the interface morphology becomes more complicated.

The phase-field method[1], provides a powerful theoretical description to free-boundary problems for phase transitions during solidification. In a free-boundary formulation, the interface is assumed to be represented as a surface and it is endowed with boundary conditions that represent the physical processes at the interface. In contrast, the phase-field method assumes the interface has a finite, but small, thickness. In addition, it postulates the existence of a function, called the phase-field, whose value identifies the phase at a particular point in space and time. The phase-field model is based on a square gradient entropy functional, which can be used to derive the socalled phase-field equations, which are a coupled pair of parabolic non-linear partial differential equations. An advantage of this approach is that the position of the interface is represented by the level sets of the phase-field and that it treats the bulk phases and interface in a uniform manner.

Phase-field models use a different approach in which a sharp interface is replaced by continuous variations which are measured by a new variable, the phase-field. This variable is governed by a partial differential equation over the entire domain and is coupled to other variables such as temperature or concentration. The position of the interface is determined by the value of the phase-field variable — the interface location does not need to be tracked explicitly. Consequently, phase-field models are easier to implement computationally than sharp-interface models, especially when complex interface morphologies are present. Phase-field methodologies for the solidification of single-phase solids for single component or pure materials were developed during 1980's. In these models, the phase-field variable is introduced in order to differentiate in a continuous fashion between the liquid and solid-phases in the system. In its simplest form, these models include a thermodynamic description of the free energy of the system as a function of the temperature and the phase-field. Phase-field models for the solidification of two-component systems having simple phase diagrams were developed in the last several years by researchers in various institutions. These models feature a free energy that depends on the solute concentration in addition to the temperature and the phase-field; the free energy is constructed in such a way that the appropriate phase diagrams for the system are recovered. The most general model includes a formulation for the free energy of the system in terms of the temperature and concentration of the system, together with two order parameters rather

* *Computer Applications Division, National Metallurgical Laboratory (CSIR), Jamshedpur 831 007, India, E-mail : skd@nmlindia.org*

than a single one. One of the order parameters, is used to indicate whether the system is in a solid or liquid phase, and the other order parameter, is used to indicate which of the two possible solid phases is present.

Phase-field models[1-4] can be divided into various intersecting classes; those that involve a single scalar order parameter and those that involve multiple order parameters; those derived from a thermodynamic formulation and those that derive from geometrical arguments. There are also formulations best suited for large deviations from local equilibrium and others for the opposite. There are physical problems where the order parameter can easily be associated with a measurable quantity such as a long-range chemical order parameter in solids and those where the order parameter is not easily measurable such as in solidification. In some cases, the method might represent real physics and in others, the method might be better viewed as a computational technique. Indeed, neither phase-field models nor sharp-interface models perfectly represent physical systems. In addition, phase-field models for solidification coupled to fluid flow are also being developed. This research should have a major impact on our understanding of flow in the mushy zone caused by shrinkage and buoyancy-driven convection.

Phase-field methods have their roots in diffuse interface theories of phase transitions developed at the beginning of the nineteenth century to model critical phenomena in fluids. The phase-field model of a solid-liquid phase transition. It is only in the last decade that they have come to the fore an alternative description of free-boundary problems, largely because computer power has only recently reached a level where phase-field methods provide a feasible method of computing realistic growth structures, such as dendrites.

The Phase-Field Approach

The classical mathematical description[1,4,6] of the solidification process has the form of a Stefan's problem, in which two diffusion equations govern the transport of heat in the solid and liquid phases, coupled by boundary conditions prescribed at the solid-liquid interface. Since the shape is changing in time it is a free boundary problem for which it has proved very difficult to find analytic solutions of practical use. For this reason a considerable effort has been put into developing numerical algorithms in the last twenty years. A single, scalar order parameter can be used to model solidification of a single-phase material. However, to employ such a simple description of the liquid-solid transition necessarily requires a number of approximations. Figure 1 shows one possible physical interpretation of a single scalar phase-field variable. The interfacial region and its motion during solidification are depicted by a damped wave that represents the probability of finding an atom at a particular location. On the left (Fig. 1), the atoms tend to be located at discrete atomic planes corresponding to the crystal. As the liquid is approached, the probability has the same average value but becomes less localised, as indicated by the reduced amplitude of the wave. Finally the probability achieves a constant value in the liquid indicating the absence of localisation of atoms to specific sites; i.e., a liquid. The amplitude of the wave might be related to the phase field.

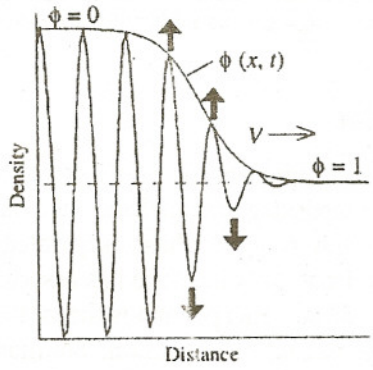

Fig. 1 : Schematic representation of a possible physical interpretation of the phase-field variable. (Adapted from ref.1).

To reduce the full description to a single phase-field variable, two simplifying assumptions are necessary. The first assumes that the amplitudes associated with the inter-atomic spacings (shortest reciprocal lattice vectors) respond to interface motion most slowly; i.e., their adjustment limits the rate of crystal growth. Amplitudes associated with shorter wavelengths, it is argued, respond more quickly. Then the description of the liquid-to-crystal transition can be reduced to a small number of amplitudes that simply describe the probability of the occupancy at the lattice positions in the three-dimensional unit cell. The second simplification comes if one assumes that the amplitudes of this limited set of Fourier components are proportional to each other. Then

a single scalar can describe the amplitude as they vary across the interface, as in Figure 1. Such a description is most appropriate for metallic systems.

This second assumption eliminates the possibility of describing anisotropy in a physical way. Interface energies are rendered isotropic. For single-variable phase-field models, anisotropy must be introduced ad hoc through an orientation dependence of the gradient energy coefficients, as shown below. Alternatively, one can keep the multiple-order parameter picture and naturally derive anisotropy[10]. If one accepts that a single-order parameter can represent the transformation from liquid to a specified solid phase, then multiple scalar phase-field variables can be used to treat situations where more than two solid phases appear, e.g., eutectic and peritectic reactions. Multiple phase-field variables can also be used to treat the multiple orientations found in a polycrystalline material[11]. From a purely mathematical point of view the phase-field parameter can be considered a tool that allows easier calculations of solidification patterns. Mathematicians refer to this as a regularisation of sharp interface problems. The sharp interface solution is called a weak solution in that it satisfies the solute and heat transport field equations in an integrated form. The only mathematical requirement to support a smooth but rapidly changing function that represents an interface is a balance between two effects: an increase in energy associated with states intermediate between liquid and solid and an energy cost.

Mathematical Formalism and Evolution Equations[1,2,11]

By demanding that the entropy always increases locally for a system where the internal energy and concentration are conserved, relationships between the fluxes of internal energy and concentration can be obtained. These are generalisations of Fourier's and Fick's laws of diffusion. A separate relationship governing ϕ is required to guarantee that the entropy increases.

$$S=\int_V\left[s(e,c,\phi)-\frac{\varepsilon_e'^2}{2}|\nabla e|^2-\frac{\varepsilon_c'^2}{2}|\nabla c|^2-\frac{\varepsilon_\phi'^2}{2}|\nabla\phi|^2\right]dV. \quad \text{.....(1)}$$

To treat cases containing interfaces, the entropy functional S is defined over the system volume V as A simpler isothermal formulation has been presented which has been appended a heat flow equation. This gives essentially equivalent results to the entropy formulation if $\varepsilon'_e = 0$.

The enthalpy density is expressed as

$$h = h_o + C_P T + L\phi, \quad \text{..... (2)}$$

where s,e,c, and ϕ are the entropy density, internal energy density, concentration and phase field, respectively, with ε'_e-ε'_c and ε'_ϕ being the associated gradient entropy coefficients. The entropy density s must contain a double well in the variable ϕ that distinguishes the liquid and solid. The quantity S also includes the entropy

$$C_p\frac{\partial T}{\partial t}+L\frac{\partial\phi}{\partial t}=\nabla.(k\nabla T), \quad \text{..... (3)}$$

which yields an equation for thermal diffusion with a source term given by where h_o is a constant; T is the temperature, C_p is the heat capacity per unit volume, which in general depends on temperature; L is the latent heat per unit volume; and k is the thermal conductivity. An isothermal treatment forms the free energy functional F, which must decrease during any process, as

$$F=\int_V\left[f(\phi,c,T)-\frac{\varepsilon_c^2}{2}|\nabla c|^2+\frac{\varepsilon_\phi^2}{2}|\nabla\phi|^2\right]dV. \quad \text{..... (4)}$$

where f (ϕ, c, T) is the free energy density, and where the gradient energy coefficients have different units than the (primed) gradient entropy coefficients used in Equation 1. For equilibrium, the variational derivatives of F must satisfy the equations,

$$\frac{\partial F}{\partial\phi}=\frac{\partial f}{\partial\phi}-\varepsilon_\phi^2\nabla^2\phi=0, \quad \text{.....(5)}$$

$$\frac{\partial F}{\partial c}=\frac{\partial f}{\partial c}-\varepsilon_c^2\nabla^2 c=\text{constant} \quad \text{.....(6)}$$

if the gradient energy coefficients are constants. The constant in Equation 6 occurs because the total amount of solute in the volume V is a constant; i.e., concentrations a conserved quantity.

$$\frac{\partial\phi}{\partial t}-M_\phi\left[\frac{\partial f}{\partial\phi}-\varepsilon_\phi^2\nabla^2\phi\right], \quad \text{..... (7)}$$

$$\frac{\partial c}{\partial t}=\nabla.\left[M_C{}^{c(1-c)\nabla}\left(\frac{\partial f}{\partial c}-\varepsilon_c^2\nabla^2 c\right)\right]. \quad \text{.....(8)}$$

The parameters M_ϕ and M_C are positive mobilities related to the interface kinetic coefficient and solute diffusion

coefficient, respectively, as described below. Equations 7 and 8 have different forms because composition is a conserved quantity and the phase-field is not. Equation 7 is called the Allen-Cahn equation, Equation 8 is the Cahn-Hilliard equation. In this formulation, the pair are coupled through the energy function $f(\phi,c,T)$. Beckermann et al.[7,8] provide another approach for obtaining the phase-field equations. This approach also includes fluid flow, but here we present the case with no flow.

$$\frac{1}{\mu_A}\frac{\delta\phi}{\delta t}=\frac{\sigma_A T_M^A}{L_A}\left[\nabla^2\phi-\frac{\phi(1-\phi)(1-2\phi)}{\delta^2}\right]-(T_M-T+m_L c_L)\left[\frac{\phi(1-\phi)}{\delta}\right]$$

The concentration equation is derived by writing the following conservation equation using phase-field weighted values for the average concentration:

$$\frac{\delta c}{\delta t}=\nabla.\left[(1-\phi)D_S\nabla_{c_S}+\phi D_L\nabla_{c_L}\right].$$

The liquid and solid concentrations can be expressed in terms of the average concentration c as where k is the solute partition coefficient. This method is particularly attractive if one does not wish to deal

$$c_L=\frac{c}{\phi+k(1-\phi)}\quad and\quad c_S=\frac{kc}{\phi+k(1-\phi)},$$

with the energy functions to determine the phase diagram. Here, only the values of T^A_M, m_L and k are required. The method also provides a sense of the relationship between terms in the phase-field equation and quantities such as the interface curvature and velocity.

Application Examples

Pioneering work in quantitative phase-field simulations of free (equiaxed) dendritic growth have been carried out[1,2,3] in three dimensions at both low undercooling (assuming local equilibrium at the interface) and at high under-cooling with the incorporation of anisotropic interface kinetic effects. In both limits, phase-field simulations have been found to be in good quantitative agreement with the sharp-interface solvability theory of dendritic growth in which the anisotropy of the interfacial energy and/or the interface kinetics plays a crucial role in determining the steady-state operating state of the dendrite tip. This is illustrated for the low under-cooling limit in Fig. 2. Convective effects on dendritic growth have been studied by a number of investigators using the phase-field method[6-9]. Fig. 3 gives an example of a two-dimensional simulation of free dendritic growth into a supercooled melt, where the melt enters at the top boundary, with a uniform inlet velocity and temperature, and leaves through the bottom boundary. The dendrite tip pointing towards the top boundary into the flow grows at a much

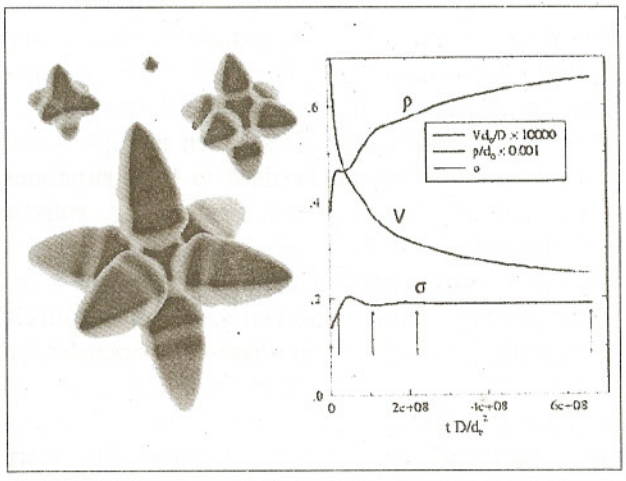

Fig. 2 : Three-dimensional dendritic growth simulation for a dimensionless supercooling of 0.05 and a 2.5% surface tension anisotropy. Snapshots of the structure are shown at the times corresponding to the arrows, and the diffusion field extends spatially on a much larger scale. (Adapted from ref. 1).

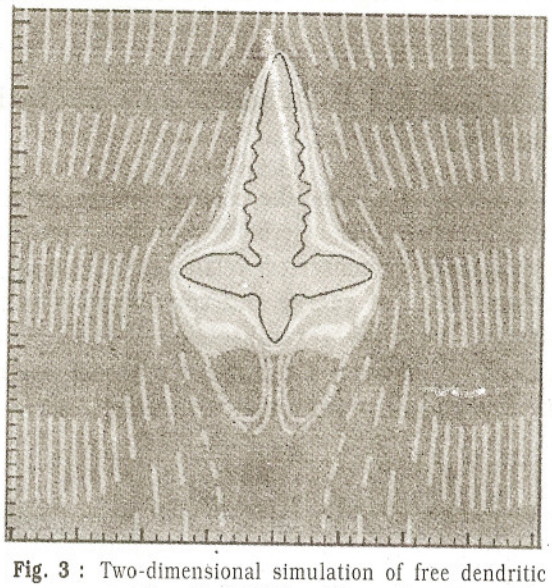

Fig. 3 : Two-dimensional simulation of free dendritic growth with fluid flow. The melt enters at the top boundary, with a uniform inlet velocity and temperature, and leaves through the bottom boundary. (Adapted from ref. 1).

faster velocity than the three other tips. The predicted heat transport enhancement owing to the flow at the upstream growing dendrite tip is in quantitative agreement with a two-dimensional Ivantsov transport theory modified to account for convection[8-9], if a tip radius based on a parabolic fit is used. Furthermore, using this parabolic tip radius, the predicted ratio of selection parameters without and with flow is found to be close to unity, which is in agreement with linearised solvability theory[10,11] for the ranges of the parameters considered. Dendritic side branching in the presence of a forced flow has also been quantitatively studied[5]. It has been shown that the asymmetric side branch growth on the upstream and downstream sides of a dendrite arm, growing at an angle with respect to the flow, can be explained by the differences in the mean shapes of the two sides of the arm. Alloy results for isothermal growth are shown in Fig. 4[1]. Such simulations were initiated with a small solid seed and a value of dimensionless supercooling of 0.86 (supercooling divided by the freezing range) and thermodynamics for a lens-shaped phase diagram. As for pure materials, simulations of dendritic growth for alloys exhibit quite realistic growth shapes. A dendrite tip radius is selected naturally from the solution to the differential equations. Simulations also show many other features common to real dendritic structures; e.g., secondary arm coarsening and microsegregation patterns. The local variation of the liquid composition as it relates to the local curvature is apparent in the mush, agreeing with that expected from the Gibbs-Thomson effect.

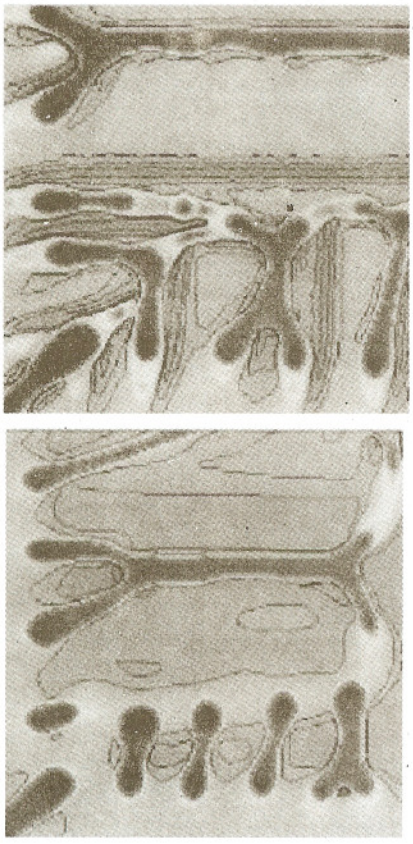

Fig. 4 : Morphologies and microsegregation patterns for isothermal alloy dendrite growth showing region deep in the mushy zone where liquid remains in the mush, (Adapted from ref. 1).

Conclusion

Compared with sharp-interface models of solidification, the phase-field method employs an extra field variable to describe whether a specific location is liquid or solid. The burden of this extra variable and its associated equation is offset by the avoidance of the mathematically difficult free-boundary problem for complicated interface shapes and the ability to handle topology changes. Realistic simulations of dendritic growth and other solidification microstructures can then be obtained using relatively simple numerical methods, although computing requirements can become excessive.

Computations of dendritic growth using the phase-field method have provided some of the most realistic simulations of this complicated phenomenon which involves an interplay between diffusion in the bulk phases and surface energy and kinetic effects at the solid/liquid interface. Simulations performed using phase-field based powerful numerical algorithms have provided a better understanding of the nature of the interaction between the various physical mechanisms and have allowed material scientists and physicists to test and modify existing simplified theories. Currently, it has been proposed to use the micro-scale study of dendritic growth via the plase-field computations to guide the development of meso-scale models which can then be employed in large-scale computations for the solidification of castings. As it has been well accepted that, casting simulations can reduce the development costs and improve the quality of cast parts.

References

1. Boettinger, W. J., Warren, J. A., Beckermann, C., and Karma, A., "Phase-Field Simulation of Solidification." Annual Review of Materials Research, Vol. 32, pp. 163-194, 2002.

2. Lu, Y., Beckermann, C. and Karma, A., "Convection Effects in Three-Dimensional Dendritic Growth," Proceedings of ASME IMECE2002, Paper No. IMECE2002-32838, Nov. 2002.

3. Ramirez, J. C., and Beckermann, C., "Quantitative Modeling of Binary Alloy Solidification with Coupled Heat and Solute Diffusion via the Phase-Field Method," 41st AIAA Aerospace Sciences Meeting, Reno, Nevada, Jan. 6-9, 2003.

4. Lu, Y., Beckermann, C. and Karma, A., "Convection Effects in Three-Dimensional Dendritic Growth," Proceedings of the 2001 Fall MRS Meeting in Boston, MA, 2001 (invited paper).

5. Tong, X., Beckermann, C., Karma, A. and Li, Q., "Phase-Field Simulations of Dendritic Crystal Growth in a Forced Flow," Physical Review E, Vol. 63, 061601 (16 pages), 2001.

6. Tong, X., Beckermann, C., and Karma, A., "Velocity and Shape Selection of Dendritic Crystals in a Forced Flow," Physical Review E, Vol. 61, pp. R49-R52, 2000.

7. Beckermann, C., Diepers, H. J., Steinbach, I., Karma, A., and Tong, X., "Modeling Melt Convection in Phase-Field Simulations of Solidification," J. Computational Physics, Vol. 154, pp. 468-496, 1999..

8. Diepers, H. J., Deckermann, C., and Steinbach, I., "Simulation of Convection and Ripening in a Binary Alloy Mush Using the Phase-Field Method," Acta Materialia, Vol. 47, pp. 3663-3678, 1999.

9. Diepers, H. J., Beckermann, C., and Steinbach, I., "A Phase-Field Method for Alloy Solidification with Convection," in Solidification Processing 1997, eds. J. Beech and H. Jones, Dept. Engineering Materials, The University of Sheffield, Sheffield, UK, 1997, pp. 426-430.

10. Tong, X., Beckermann, C., and Karma, A., "Phase-Field Simulation of Dendritic Growth with Convection," in Modeling of Casting, Welding and Advanced Solidification Processes VIII, eds, B.G. Thomas and C, Beckermann, TMS, Warrendale, PA, 1998, pp. 613-620.

11. Diepers, H. J., Beckermann, C., and Steinbach, I., "Modeling of Convection-Influenced Coarsening of a Binary Alloy Mush Using the Phase-Field Method," in Modeling of Casting, Welding and Advanced Solidification Processes VIII, eds, B.G. Thomas and C. Beckermann, TMS, Warrendale, PA, 1998, pp.565-572.